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DETERMINATION OF THE CONCENTRATION OF WATER-SOLUBLE SALTS IN SOILS ON THE BASIS OF THE COEFFICIENT OF ELECTRICAL CONDUCTIVITY

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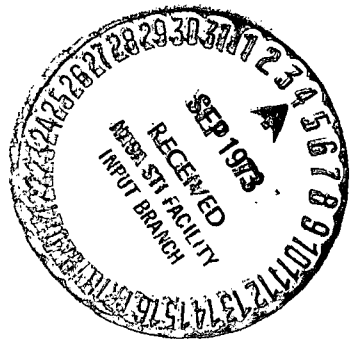
Translation of "Opredeleniye kontsentratsii vodnorastvorimykh soley v pochvakh po koeffitsientu elektroprovodnosti," Izvestiya Timiryazevskoy Sol'skokhozyaistvennoy Akademii, No. 6, 1967, pp. 136-140.



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16. Abstract

While the measured conductivity of Solonetzic Chestnut soils is approximately the same as that predicted on the basis of conductivity of electrolytes contained therein, that of Solonetz soils is much higher than the theoretical, for reasons poorly understood.

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DETERMINATION OF THE CONCENTRATION OF WATER-SOLUBLE SALTS IN SOILS ON THE BASIS OF THE COEFFICIENT OF ELECTRICAL CONDUCTIVITY

S. N. Aleshin and G. A. Slovtsova

The salt content of the soil is usually estimated on the basis of the salt concentration in the water extracts. /136* There are various methods for determining the salinity of soils and natural water based on dry residue, the density of solutions, refraction, quantitative chemical analyses, and electrical conductivity. Numerous investigators have made use of the last method [1, 2, 3, 4, 5, 6, 9, etc.]. It is very useful when there is no need to separate the salt content into its component parts.

The electrical conductivity of solutions of electrolytes is indicated by the specific electrical conductivity $\varkappa$, measured in $ohm^{-1} \cdot cm^{-1}$, which is related to the normal ionic concentrations (c_i) using the following formula:

$$1000\varkappa = c_i(l_k + l_a), \quad (1)$$

where kappa is the specific electrical conductivity (in mhos); c_i is the ionic concentration of the solution (geq/l), and l_k and l_a are the electrolytic mobility of the cation and anion.

The electrical conductivity of solutions is governed by the presence of ions in them. In the case of weak electrolytes, which dissociate only partially into ions and are present in solutions chiefly in the form of molecules, the concentration of the substance determined by the method of electrical conductivity will not coincide with the concentration as determined by other analytical methods.

*Numbers in the margin indicate pagination in the foreign text.

Aqueous soil extracts are mainly solutions of strong electrolytes. Strong electrolytes, which with few exceptions include all salts regardless of the strength of their parent acids and bases, dissociate completely into ions in water solutions. A sphere of ions of opposite sign forms around each ion. Hence, when an electrical current is passed through the solution, the speed of the ions, and therefore the electrical conductivity, will depend not only on the applied voltage but also on the energy of interaction of the oppositely charged ions. It is evident that the higher the density of the sphere around the ions, the lower will be their electrolytic mobility. And since ion mobilities are usually considered to be constant values, with a given electrical conductivity the decline in mobility of ions is expressed in eq. (1) as a decrease in the ionic concentration c_i. Therefore, in calculating the properties of strong electrolytes, A is /137 used instead of c_i, i.e. the ionic activity in a given solution, which is related to the normal concentration (c) by the simple expression:

$$A = c \cdot f, \tag{2}$$

where f is the activity coefficient.

The activity represents the effective concentration of electrolytes by indicating the total influence of the mutual attraction of the various ions, the phenomenon of ion hydration, and other effects. The electrolyte activity coefficient for infinitely dilute solutions is equal to unity, and for other solutions it is usually less than one.

If, instead of c_i, we substitute in eq. (1) its equivalent value of A from expression (2), we obtain the following expression:

$$1000\varkappa = c \cdot f (l_к + l_а), \tag{3}$$

and therefore

$$c = \frac{1000\varkappa}{f(l_K + l_a)}. \qquad (4)$$

Hence, in order to calculate the salt concentration in any solution on the basis of its electrical conductivity using eq. (4), one must know the value of the activity in this solution.

It is not difficult to determine the activity coefficient for particular ions and solutions of individual electrolytes. This may be accomplished not only by the method of electrical conductivity (in this case the activity coefficient is designated the electrical conductivity coefficient), but also on the basis of the electromotive force, on the basis of freezing point depression, and on the basis of osmotic pressure. It is quite difficult, however, to determine the activity coefficient in solutions of mixed salts with different types of valences.

In their effort to solve this problem G. Lewis and M. Randall [7] introduced a new term, ionic strength μ

$$\mu = \frac{1}{2}(m_1 \cdot z_1^2 + m_2 \cdot z_2^2 + m_3 \cdot z_3^2 + \ldots), \qquad (5)$$

where m is the molar concentration of the ion and z in its valence.

The same authors also formulated the principal that: "Except for concentrated solutions, the activity coefficients of a particular electrolyte depends not on the characteristics of any other strong electrolyte which may be present in the solution, but only on the total ionic strength."

TABLE 1. ACTIVITY COEFFICIENTS OF IONS OF DIFFERENT VALENCES (according to [8])

Ions	Values of f with ionic strength μ,					
	0,001	0,005	0,01	0,05	0,1	0,2
monovalent	0,97	0,93	0,90	0,81	0,76	0,70
divalent	0,87	0,74	0,66	0,44	0,33	0,24
trivalent	0,73	0,51	0,39	0,16	0,08	0,04

Approximate values of activity coefficients for ions of different valences are given in Table 1 as a function of ionic strength.

One can calculate the activity coefficients for a mixture of electrolytes of different valence types by using the following equations (from [7]):

$$\lg f = -\frac{0{,}507 \cdot z_1 \cdot z_2 \sqrt{\mu}}{1 + \sqrt{\mu}}, \quad (6)$$

where z_1 and z_2 are the valences of the corresponding ions; and μ is the ionic strength.

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TABLE 2. BRIEF DESCRIPTION OF THE PHYSICAL CHEMISTRY OF THE SOILS STUDIED

Soil	Depth, cm	pH of water extract	tot. concent. of salts in the water extract, meq/l	specific electrical conductivity, mhos	
				$K_{exp.}$	$K_{theor.}$
Solonetzic Chestnut soil, profile No. 7	0—10	6,9	3,12	$1{,}89 \cdot 10^{-4}$	$2{,}86 \cdot 10^{-4}$
	17—27	7,0	3,48	$2{,}04 \cdot 10^{-4}$	$3{,}26 \cdot 10^{-4}$
	30—40	7,3	3,94	$2{,}25 \cdot 10^{-4}$	$3{,}64 \cdot 10^{-4}$
	60—70	7,9	4,14	$1{,}34 \cdot 10^{-4}$	$3{,}80 \cdot 10^{-4}$
Medium steppe virgin Solonetz, profile No. 1	0—10	7,7	3,34	$2{,}42 \cdot 10^{-4}$	$3{,}17 \cdot 10^{-4}$
	15—25	8,2	6,99	$4{,}60 \cdot 10^{-4}$	$6{,}25 \cdot 10^{-4}$
	27—37	8,3	9,41	$6{,}20 \cdot 10^{-4}$	$8{,}50 \cdot 10^{-4}$
	40—50	8,4	13,15	$8{,}90 \cdot 10^{-4}$	$12{,}30 \cdot 10^{-4}$

The coefficient of electrical conductivity (f_e) can be determined on the basis of the experimentally determined data concerning the specific electrical conductivity of the

aqueous soil extracts and the chemically determined salt content. If f_e is stable for particular kinds of soils, then the concentration of salts in the water extract under the conditions of determination of its electrical conductivity can be calculated directly using eq. (4).

Our studies were based on samples of Solonetzes and Solonetzic Chestnut soils collected from profiles at the Volgograd Oblast Agricultural Station. The samples of Solonetzic Chestnut soils were taken from a Solonetzic area which has been under biological melioration for 12 years, and the Solonetz samples were taken from the same area but from virgin soil (i.e. the virgin Solonetzes are the original form of the present Solonetzic Chestnut soils).

The specific electrical conductivity was determined using a Kohlrausch bridge in two replications and two parallel samples at 18° C. At the same time the same water extracts were analyzed chemically.

The possible theoretical electrical conductivity was calculated on the basis of the ionic concentration (c_i), determined by the chemical analytical method, and the electrolytic conductivity of the corresponding ions [8]:

$$1000\varkappa = (c_{HCO_3^-} \cdot l_{HCO_3^-}) + (c_{SO_4^{--}} \cdot l_{SO_4^{--}}) + (c_{Cl^-} \cdot l_{Cl^-}) + (c_{Ca^{++}} \cdot l_{Ca^{++}}) + (c_{Mg^{++}} \cdot l_{Mg^{++}}) + (c_{Na^+} \cdot l_{Na^+}). \quad (7)$$

The data obtained are given in Table 2.

The quotient resulting from dividing the value of experimental $\varkappa$ by the value of theoretical $\varkappa$ will be the total average coefficient of electrical conductivity f. The

ionic strength μ was calculated using the eq. (5), and then the activity coefficient f was determined using eq. (6) (see Table 3).

TABLE 3. EXPERIMENTAL AND THEORETICAL ACTIVITY COEFFICIENTS

Soil	Depth, cm	ionic strength, μ	activity coefficients	
			f_e	f_T
Solonetzic Chestnut soil, profile No. 7	0—10	0,0022	0,66	0,66
	17—27	0,0025	0,63	0,60
	30—40	0,0028	0,62	0,57
	60—70	0,0029	0,62	0,57
		Average	0,63	0,60
Medium Steppe Virgin Solonetz, profile No. 1	0—10	0,0021	0,75	0,61
	15—25	0,0041	0,74	0,51
	27—37	0,0054	0,73	0,47
	40—50	0,0075	0,72	0,47
		Average	0,74	0,51

The experimentally determined electrical conductivity coefficients for the Solonetzic Chestnut soil were approximately the same over the entire profile and were close to the theoretically calculated value. As far as the stability of f_e in the Solonetzic Chestnut soil is concerned, calculations based on 20 samples showed that it averaged 0.63 for an ionic strength of 0.002-0.004 (out of a total of 20 samples a maximum deviation of 7 percent was observed in three cases).

In the Solonetzes f_e was 0.74, which was significantly higher than the average activity coefficient calculated on the basis of ionic strength. This can be explained, in /139
our opinion, by the high degree of dispersion of the soil absorbing complex in the Solonetzes and the substantial content of colloids in the water extract. This situation probably causes an increase in the electrical conductivity with a corresponding increase

in the value of f_e. It is known that colloidal particles affect electrical conductivity [5]. Solonetzes also have a high pH (see Table 2), and this also affects electrical conductivity. The mobility of hydroxyl ions was not taken into account.

In order to determine the concentration of water-soluble salts in soils using eq. (4), in addition to finding the electrical conductivity coefficient, one must also know the value of the average electrolytic mobility of ions ($l_k + l_a$). The value which we calculated on the basis of experimental data for Solonetzic Chestnut Soils and Solonetzes ($l_k + l_a$) was 92.5. Hence, knowing the value of f_e and ($l_k + l_a$), we can determine the concentration of salts in the soils using eq. (4). The salt concentrations in water extracts as determined by us using eq. (4) and as determined chemically are presented in Table 4.

TABLE 4. CONCENTRATION OF SALTS IN THE SOIL, DETERMINED CHEMICALLY AND ON THE BASIS OF ELECTRICAL CONDUCTIVITY

Soil	Depth, cm	specific elec. conductivity, K	salt concen., meq/l	
			as deter. by chem. anal.	as deter. by elec. conduc.
Solonetzic Chestnut, profile No. 7	0—10	$1,89 \cdot 10^{-4}$	3,12	3,24
	17—27	$2,04 \cdot 10^{-4}$	3,48	3,49
	30—40	$2,25 \cdot 10^{-4}$	3,94	3,86
	60—70	$2,34 \cdot 10^{-4}$	4,14	4,01
Solonetzic Chestnut, profile No. 21	0—10	$1,65 \cdot 10^{-4}$	2,88	2,82
	20—30	$2,08 \cdot 10^{-4}$	3,64	3,57
	40—50	$2,28 \cdot 10^{-4}$	4,02	3,91
Medium Steppe Virgin Solonetz, profile No. 1	0—10	$2,42 \cdot 10^{-4}$	3,34	3,59
	15—25	$4,60 \cdot 10^{-4}$	6,99	6,82
	27—37	$6,20 \cdot 10^{-4}$	9,41	9,20
	40—50	$8,90 \cdot 10^{-4}$	13,15	13,20

The concentration of salts in the Solonetzic Chestnut soil and the Solonetzes, as /140 calculated in the basis of the electrical conductivity coefficient, was close to that de-

termined chemically.

CONCLUSIONS

1) It was established experimentally that the electrical conductivity coefficient of Solonetzic Chestnut soils with an ion strength of 0.002-0.004 was equal to 0.63 on the average and was close to that calculated theoretically (0.60). The concentration of water-soluble salts from these soils, as determined on the basis of electrical conductivity was close to the concentration determined chemically.

2) The experimentally determined coefficient of electrical conductivity for Solonetzes (0.74) was significantly higher than that calculated theoretically (0.51). The applicability of this electrical conductivity coefficient for calculations of the concentrations of water-soluble salts in Solonetzes of different kinds requires further study.

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